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The effect of material purity on the optical and scintillation properties of solution-grown *trans*-stilbene crystals

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Abstract

Large, 10 cm-size, single crystals of *trans*-stilbene were grown for the first time from solution by a temperature reduction technique. Their scintillation performance for fast neutron detection depended on the purity of the initial starting material. A light-yield-inhibitor-free starting material was specially synthesized and crystals from this material were compared to those grown from commercially available powders of *trans*-stilbene. The use of pure material made possible the growth of the large size crystals (>400 g) with excellent neutron gamma discrimination performance, which are needed for use as radiation detection material.

Key Words: B1. Organic crystals, A2. Solution growth, B1. *trans*-Stilbene, B2. Organic scintillator, B3. Neutron detection, B3. Pulse shape discrimination

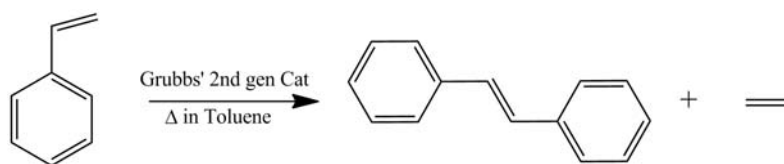
1. Introduction

Trans-stilbene is a well-known scintillation material which is used for the detection of high-energy neutrons in the presence of strong gamma radiation because of its excellent neutron-gamma pulse shape discrimination (PSD) properties [1, 2]. As for most organic crystals, *trans*-stilbene is traditionally grown from melt by the Bridgman technique. This method works well for

high-symmetry crystals, but for highly anisotropic crystals of the monoclinic system with a proclivity to cleavage, to which *trans*-stilbene belongs, has challenges including stress and cracking during growth and cooling, with a resulting limit to the final size of the crystal. When large volume single crystals are needed, low-temperature solution growth may offer advantages in the scaling process. However, as for all scintillation crystals grown from melt or solution, one of the most important conditions is the use of high-purity starting material free of any light-absorbing contaminants that can incorporate into the crystals causing a loss of scintillation light yield (LY). *Trans*-stilbene powder is commercially available from many sources at 96-99% purity at a relatively low cost. However, as shown in our multiple experiments, even at the highest purity, all commercial materials have insufficient purity, always containing LY-inhibiting impurities that could not be removed by re-crystallization, column chromatography, zone refining, or sublimation. As a result, crystals grown from this material had LY at least 2-fold lower than commercial melt grown crystals of the same size. In this particular work, the problem was resolved by the use of an alternative synthetic route that produced *trans*-stilbene starting material with a substantially decreased concentration of LY-inhibiting contaminants that enabled production of solution-grown crystals with the scintillation performance not worse than in the best available melt-grown samples. This paper presents a comparison of the optical and scintillation properties (LY and PSD) of crystals grown from materials of different purity, giving at the same time a description of the first experiments on large-scale solution growth of high-quality *trans*-stilbene single crystals.

2. Materials and characterization techniques

Trans-stilbene is available for purchase from many companies (Aldrich, Alfa Aesar, Acros Organics, TCI America and others). Independent of the listed purity, all commercial batches had a slight yellow color upon dissolution. As a first step to purifying the commercial material, initial powders were re-crystallized from toluene 4-6 times and dried prior to solution preparation. Alternative starting material for comparative studies was synthesized using either the Grubbs 2nd generation ([1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium) or the Hoveyda- Grubbs 2nd generation (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)dichloro(*o*-isopropoxyphenylmethylene)ruthenium) catalyst, according to the following reaction [3].



In this synthesis, the solvent (toluene or triethylcitrate) and reactant (styrene) were degassed by sparging with nitrogen three times at 15 min intervals. Then the catalyst was added at between 0.01-0.1 mol %. The reactions were monitored by thin layer chromatography and depending on the scale were run from 3-8 hrs. The yields from both catalysts were 80-85%. Re-crystallization from toluene removed the catalyst and any minor bi-products.

Anhydrous anisole (Aldrich, 99.7%) was chosen as the solvent for the preparation of the final growth solutions because of its high (154 °C) boiling point and low vapor pressure (10 mm Hg at 42.2 °C). Purity of the *trans*-stilbene crystals and powders was determined by absorption spectra measured with a Shimadzu UV-2401PC spectrophotometer, photoluminescence (PL) spectra measured with UV excitation using a Fluoromax-2 spectrometer, and by gas

chromatography/mass spectrometry (GC/MS) measured with an Agilent 6890N GC and Agilent 5975c MS.

Light yield measurements of stilbene crystals were carried out with ^{137}Cs source emitting γ -rays with the energy of 662 keV. Scintillator samples wrapped in Teflon and black tape to ensure system tight to ambient light were coupled to a 2-inch R6231-100 Hamamatsu photomultiplier using optical grease. Signal from the photomultiplier base was transmitted to a 14-bit, 200 MHz 14200Gage digitizer. Full waveforms were archived for offline analysis. The relative scintillation LY was evaluated from the position of the Compton edge in the ^{137}Cs spectra, in which 500 keV electron-equivalent was defined by 50% of the Compton edge peak. Neutron detection and neutron-gamma discrimination properties of samples were studied using a ^{252}Cf source as in [4]. Quantitative analysis of neutron-gamma pulse shape discrimination was made by comparison of PSD figures of merit, $\text{FOM} = S/(\sigma_{\text{gamma}} + \sigma_{\text{neutron}})$, where S is the separation between gamma and neutron peaks, and σ_{gamma} and σ_{neutron} are Full Width Half Maxima (FWHM) of the corresponding peaks. Since both LY and PSD depend on the crystal dimensions, comparison was made with samples of the same size and shape.

Crystals were grown by a well-established temperature reduction technique developed previously for growth of KDP crystals from water [5] and recently modified for growth of molecular crystals from organic solvents [6].

3. Results and Discussion

3.1. Solubility measurements

In order for any crystal to be grown from solution it must be reasonably soluble in the solvent of choice and stable in the solution. For growth by temperature reduction, the material should

also have significantly higher solubility with increasing temperature. *Trans*-stilbene meets these criteria. In low-temperature solution growth, the relative supersaturation, $\sigma = (C - C_0)/C_0$, where C and C_0 are the actual and equilibrium (solubility) solute concentrations in the growth solution, is the most important parameter for control of the growth rate. For the growth of the first *trans*-stilbene crystals, we have used the common practice of slow growth by temperature reduction, at which $\sigma > 0$ required for crystal growth was created by an approximately estimated temperature drop that was gradually increased with the crystal size. In the future, for more rapid growth, much better control is planned to be achieved by more precise monitoring of the supersaturation, taking into account both the solubility and the gradually increasing crystal mass [6]. However, both slow and rapid growth require knowledge of the temperature dependence of solubility not reported previously for *trans*-stilbene in any organic solvent.

Since *trans*-stilbene, as for many organic compounds, can sublime upon heating, it was not possible to use the standard technique of weighing solutions before and after drying to determine the equilibrium concentration. Instead, to obtain solubility data in the temperature range of crystal growth, solutions containing a known amount of solid powder and solvent were stirred in a sealed crystallizer for 1-2 days. The temperature was adjusted until a small piece of added crystal neither grew nor dissolved. The equilibrium concentrations obtained from this method are accurate within 0.1 °C. Figure 1 presents the results of *trans*-stilbene solubility in anisole for a temperature range of 25-60 °C which is typically used for solution crystal growth by the temperature reduction method.

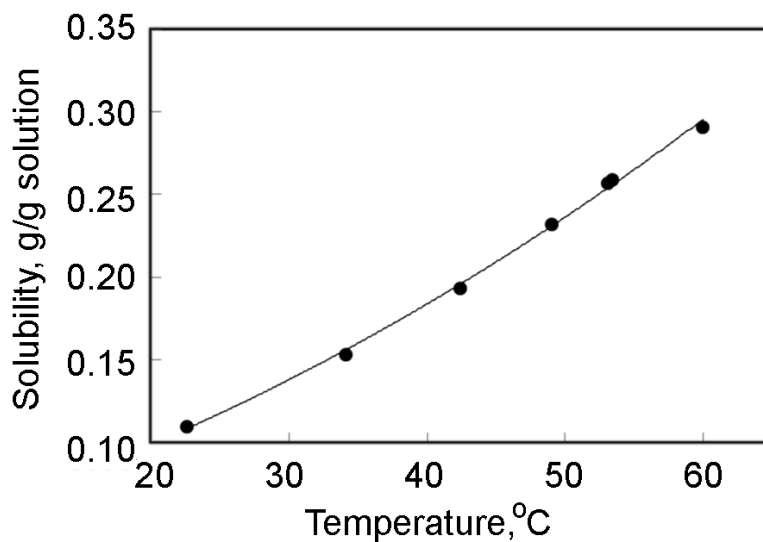


Figure 1. Experimentally measured values of *trans*-stilbene solubility in anisole solution. For interpolation, a second order polynomial equation, $y = 3E-05x^2 + 0.0022x + 0.0421$, fits the data with $R^2 = 0.998$.

3.2. Crystal growth

As described previously [6], an initial seed obtained from a small crystal grown by the room temperature evaporation method was glued into the hole in the center of an aluminum platform. Typical growth runs started in solutions with initial saturation temperatures of approximately 50°C. The platform with the seed was heated and loaded into a crystallizer about 7°C above the saturation temperature. The temperature was gradually lowered to 0.1-0.2°C below saturation temperature for growth. The larger crystals generated by this method were then used to prepare better seeds for further growth experiments. The initial growth runs were conducted using

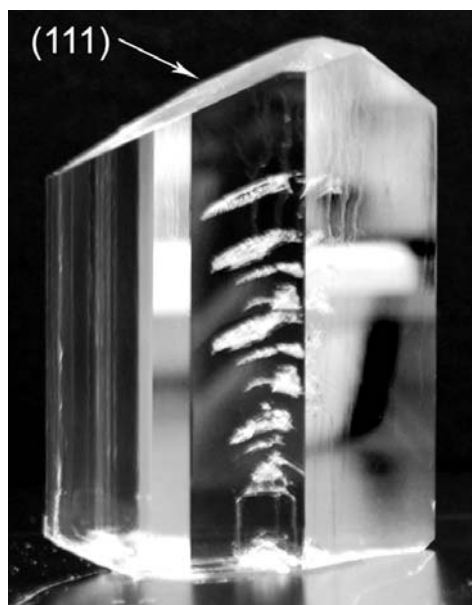


Figure 2. Trans-stilbene single crystal (~10 cm in height) grown in anisole on a “point” seed with repeating inclusions in the {111} growth sectors.

“point” seeds with a size of 10-15 mm in height. Despite the fact that such seeds did not have any visible defects, growth of fully faceted crystal always resulted in formation of repeating solution inclusions in the {111} growth sectors (Figure 2), unless crystals were grown at extremely slow growth rates. The issue of solution inclusions was avoided by the elimination of the {111} growth sectors. To obtain inclusion-free crystals, growth was begun with longer seeds, using a specially designed platform that consisted of a base and a top disc separated by a distance equal to the desired height of the final crystal (10 cm in Figure 3). Slightly shorter seeds with a length of 9-9.5 cm were cut with a diamond wire saw with at least one natural facet preserved to insure the correct orientation along the monoclinic b-axis. The other three sides of the seed were carefully polished with toluene to create a uniform cross-section of a rhomb with the pairs of facets parallel to the pinacoids of a naturally faceted *trans*-stilbene crystal, as shown in Figure 3 A.

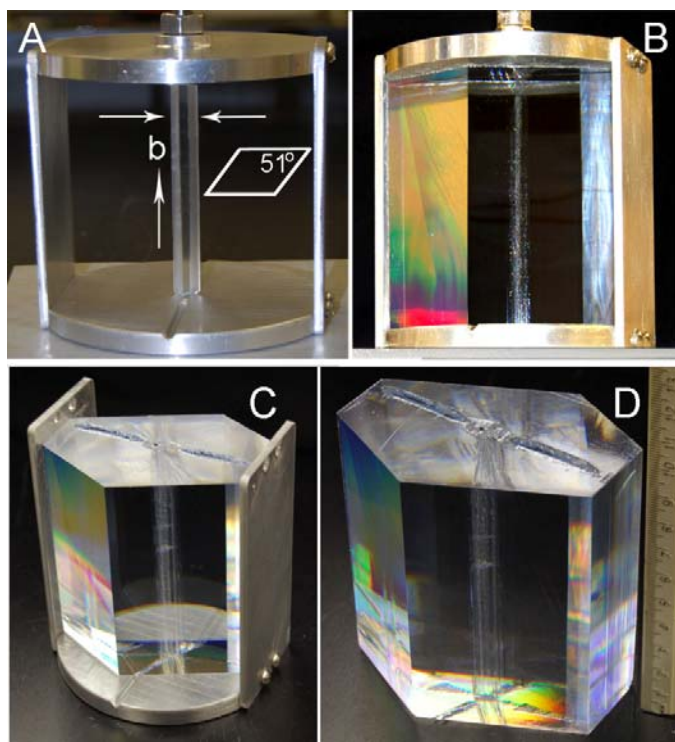


Figure 3. A trans-stilbene crystal grown with restriction in vertical and horizontal directions: (A)-Initial seed cut along the monoclinic b -axis, with length close to the corresponding size of the final crystal. Rhomboid schematic illustrates the horizontal cross section of the seed cut and polished with the vertical sides close to the orientation of the natural facets of a trans-stilbene crystal. (B)-a full-grown crystal on an assembled platform after removal from the solution; (C)-a stage of the platform disassembling; (D)-final 10 cm-long single crystal.

Care was taken to keep the correct orientation of the seed during epoxy gluing [7]. The seed was placed between the platform base and the upper flat disc so that shortly after the beginning of growth the crystal's top would be restricted by the upper plate. Growth would then proceed by the advancement of the vertical pinacoids. Since these facets typically did not produce any inclusions, they could then be grown faster. Grooves on the platform base and on the upper plate helped hold the crystal in place, preventing its movement during reversible rotation. The initial vertical growth was measured using a telescopic device while the horizontal dimensions were measured with a 5 mm-spaced grid etched on the platform surface.

After the seed was loaded into the crystallizer, it was held for at least 30 minutes slightly above saturation temperature so that any free particles of *trans*-stilbene on the seed were dissolved to insure spontaneous nucleation-free growth [8]. The seed was only allowed to dissolve slightly and growth started slowly (1-2mm/day) until the crystal touched the top plate. No inclusion formation was observed once the crystal was constrained by the top disc, allowing for a slight acceleration of growth rate to 2-4 mm/day in the horizontal direction. In addition to constraining the upper portion of the crystal, it is of benefit to constrain the sharp edges between the vertical facets of the crystals as well by growing them into wide bars (Figure 3 B). This makes the crystals less fragile and easier to handle after growth. The use of a platform with a design which facilitates the assembly/disassembly process allows for easy removal of the crystals at room temperature after growth is accomplished (Figure 3 C and D).

3.3. Comparison of crystals of different purity

A specific feature of all *trans*-stilbene crystals grown in the present work from commercially available powders was a slight blue-gray color not observed in any of the available samples (10) of commercial melt-grown crystals (ScintiTech, Inc.) of similar size. More detailed comparisons always showed inferior LY that at increasing size and more visible coloration became more than a factor of two lower in solution-grown crystals (Figure 4).

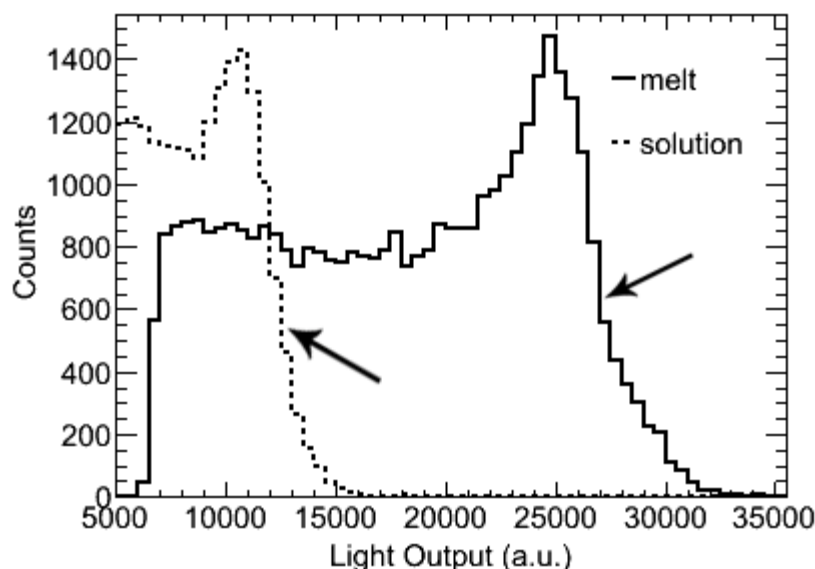


Figure 4. Relative ^{137}Cs LY showing more than twice lower LY in solution-grown (Aldrich material) crystals (dashed line) in comparison to the melt-grown *trans-stilbene* crystals (ScintiThech, Inc)(solid line). Arrows show the position of the Compton edge used for comparison. Same size $2 \times 2 \times 1$ (cm^3) samples were used for the measurements.

It should be noted that independent of the source, all commercial *trans-stilbene* powders exhibited very similar PL spectra always slightly red-shifted compared to those reported previously for purified *trans-stilbene* [9,10] and measured in the present work with melt-grown crystals. Multiple attempts made to purify the commercial powders by further re-crystallization, sublimation, column chromatography, and zone refining did not produce any substantial changes in the spectra of the treated powders and still yielded slightly colored, low-LY crystals in growth experiments. Noticeably different results were obtained with the alternative Grubbs catalyst synthesized *trans-stilbene*.

The first difference indicating the positive effect produced by the use of purer starting material is illustrated by Figure 5, which shows a visible difference in the color of the crystal

grown from pure material in contrast to a *trans*-stilbene crystal grown from the standard commercially available material. Comparison of the two crystals presented in Figure 5 clearly

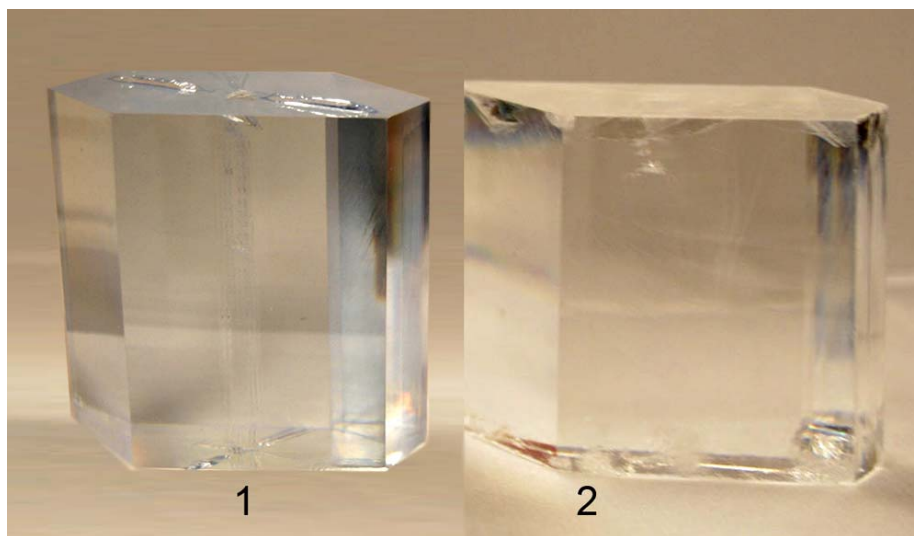


Figure 5. Trans-stilbene single crystals grown from anisole solution using (1) regular commercial and (2) synthesized trans-stilbene. The height of the crystals is about 5 cm.

shows that the coloration typical for all crystals grown from commercial (Aldrich) material is absent in a crystal grown from the Grubbs catalyst synthesized *trans*-stilbene powder.

A more detailed comparison of the optical properties was made with plates of the same thickness (1 cm) and area (about 5cm x 5cm) cut from the two crystals. Figure 6 presents corresponding absorption and PL spectra measured in the UV-visible region. As indicated by Figure 6 A and B, the crystal grown from the commercial material shows absorption bands absent in the plate cut from the crystal grown from the synthesized *trans*-stilbene. Noticeable differences could also be observed in the PL spectra. As shown in Figure 6 C and D, the peaks of the spectra of the crystal grown from the synthesized material shifted to the region of shorter wavelength compared to the crystals grown from Aldrich material. It should be noted that the

peak position, as well as the shape of the spectra obtained with the new crystals practically coincided with the PL spectra measured in the melt-grown stilbene samples (not shown in Figure 6 for clarity of presentation).

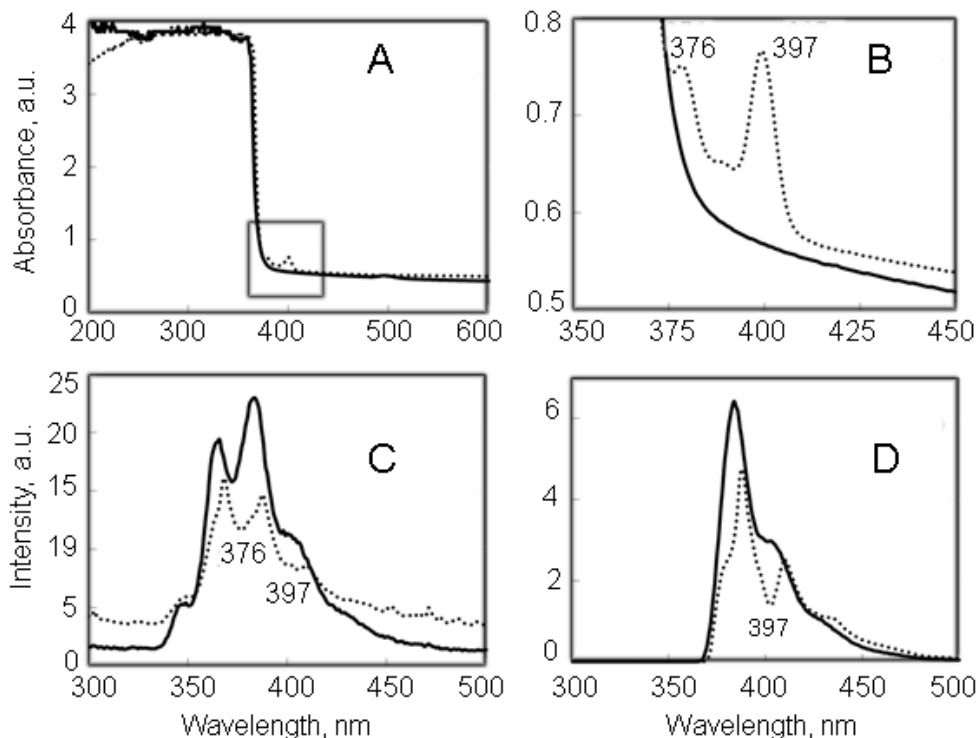


Figure 6. Absorption and fluorescence spectra obtained with 1 cm thick plates cut from the crystals grown from the Aldrich (dashed) and the Grubbs-catalyst synthesized (solid) materials: (A)-total absorption in UV-visible region; (B)-absorption corresponding to the squared inset of spectra A; (C)-photoluminescence spectra taken by reflection from the plates surface; (D)-corresponding spectra measured by transmission through the plate thickness. The excitation wavelength is 273 nm.

GC/MS chemical analysis of the crystals grown from synthesized and commercially available materials showed the presence of many impurities that had incorporated into the crystals (Figure 7). Both crystals were >99% *trans*-stilbene when all peaks were considered

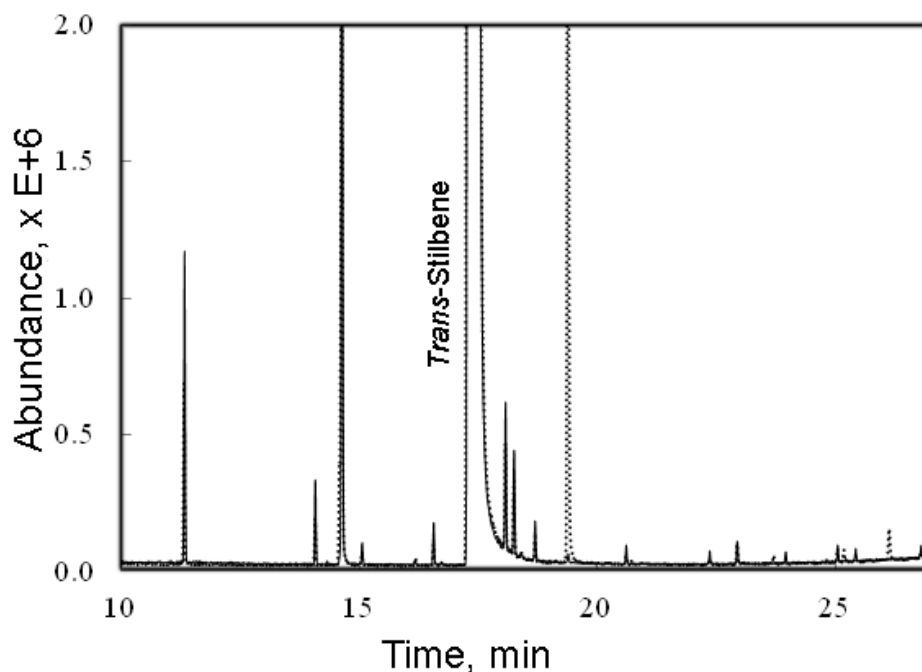


Figure 7. Comparative results of GC/MS chemical analysis obtained on material from crystals grown from Aldrich (dashed) and Grubbs catalyst synthesized (solid) *trans-stilbene* powders.

using total ion counts (tic). However, when the crystal from synthesized material was compared to the crystal from commercial material, the absence of one main peak was observed. This contaminant (RT = 19.367) appears to be 2-phenylindene based on the NIST08 library and confirmed by chromatography of an authentic standard. It is present in the crystal grown from commercially available material at approximately 0.5% tic. However, small crystals grown at room temperature by evaporation from synthesized *trans-stilbene* doped with 2-phenylindene at 1-2 wt% showed LY similar to un-doped crystals from the same material demonstrating that 2-phenylindene is not the LY-inhibiting contaminant. V.A. Averin *et al.* indicated that the LY inhibiting impurity is probably 1-methylphenanthrene [11]. However, no evidence of any of the isomers of methylphenanthrene was seen in crystals from either commercial or synthesized materials or in the initial powders with a detection limit of <10 ng/mg sampled. The LY

inhibiting compound may be one of the other smaller peaks shown in Figure 7 or may be some other compound which is not amenable to our GC method or GC chromatography in general. The fact that the absorption bands shown in Figure 6 A and B coincide with the positions of the valleys in the emission spectra of the impure stilbene (Figure 6 C and D) indicates that the ~ difference in the spectra results from the spectral distortion caused by the presence of non-fluorescent impurities different in their structure from stilbene, 2-phenylindene, or 1-methylphenanthrene. While the detection of the precise nature of the contaminant responsible for the loss of the LY may still present a subject for further studies, its relevance to the production of better performance *trans*-stilbene crystals seems less significant because the alternative synthesis produced LY-inhibiting-contaminant-free starting material.

3.4. Neutron detection properties

Characterization studies performed with plates from the two *trans*-stilbene crystals confirmed that the decreased level of absorption obtained in crystals grown from purer material leads to a sharp improvement of the scintillation properties of stilbene crystals grown from solution. The results of scintillation LY measurements comparing plates from *trans*-stilbene crystals grown from synthesized and commercially available materials are presented in Figure 8.

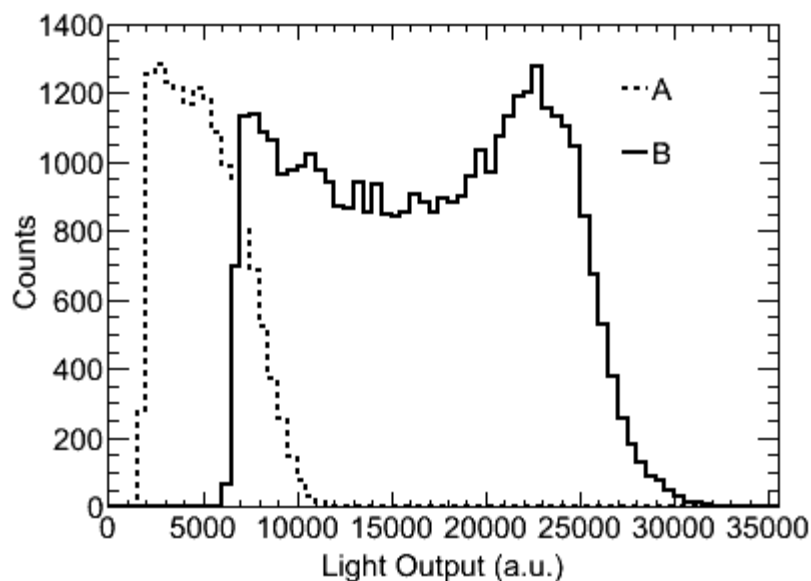


Figure 8. Relative ^{137}Cs LY measured in the $5 \times 5 \times 1$ (cm^3) plates cut from the *trans*-stilbene crystals grown from the Aldrich (A) and the Grubbs-catalyst synthesized (B) materials shown in Figure 5.

They show that the use of higher-purity starting material leads to a dramatic increase in the LY collection (from $\sim 25,000$ a.u. to $\sim 8,000$ a.u. in a crystal grown from Aldrich material). The similarity of the LY in the crystal from specially synthesized material to that measured in melt-grown crystals (see Figure 4) showed that the low LY in the first solution-grown crystals did not relate to the method of growth, but was rather determined by the presence of light-inhibiting impurities. Corresponding measurements made with a ^{252}Cf source, that produces both gamma rays and high-energy neutrons, shows similar enhancement in the neutron/gamma pulse shape discrimination indicated by the sharp increase of PSD FOM from 2.47 to 4.25 (Figure 9) at the ^{137}Cs Compton edge energy, $480 \pm 75 \text{ keV}$. The latter value of FOM = 4.25 is close to that reported for commercial melt-grown stilbene crystals (4.7 in Ref. 4), showing that, when pure

material is used, solution-grown crystals may have as high scintillation performance as stilbene crystals produced by more traditional growth techniques.

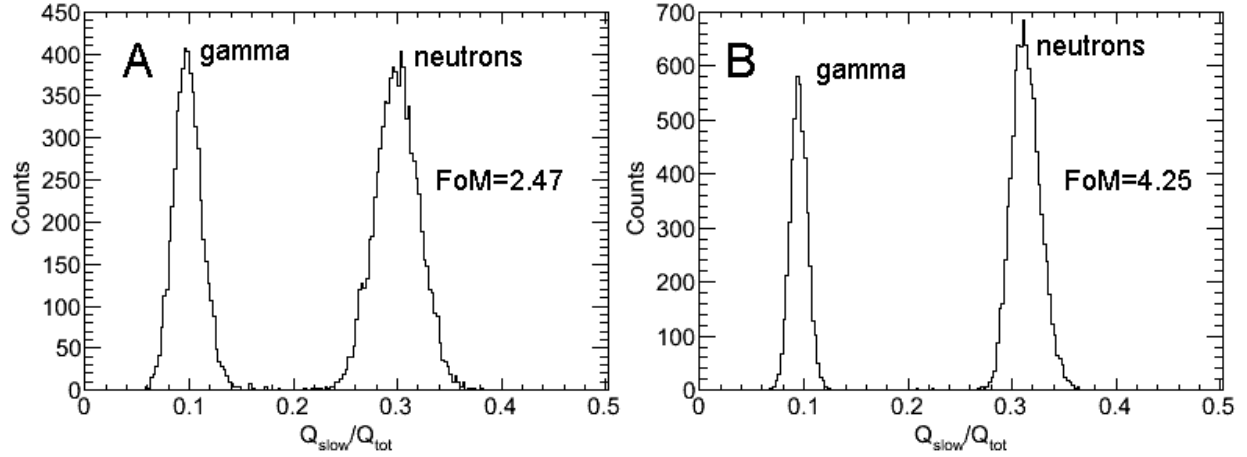


Figure 9. Comparison of PSD measured with two $5 \times 5 \times 1$ (cm^3) plates cut from *trans*-stilbene crystals grown from the Aldrich (A) and the Grubbs-catalyst synthesized (B) materials shown in Figure 5. Figure of merit values were calculated in ^{137}Cs Compton edge energy domain, $480 \pm 75 \text{ keV}$.

Conclusion

Single crystals of *trans*-stilbene were grown from anisole solution by the temperature reduction method. By using constrained growth, large, essentially inclusion-free crystals were grown at a moderate growth rate of 2-4 mm day. Use of LY inhibitor-free initial starting material is essential to good optical quality. Characterization of the scintillation properties of crystals from specially synthesized *trans*-stilbene indicate that, similar to traditional melt-grown stilbene, these crystals can be used as efficient PSD materials for high-energy neutron detection in the presence of gamma radiation background.

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